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Survey of Industrial Hazard Anticipation Technology

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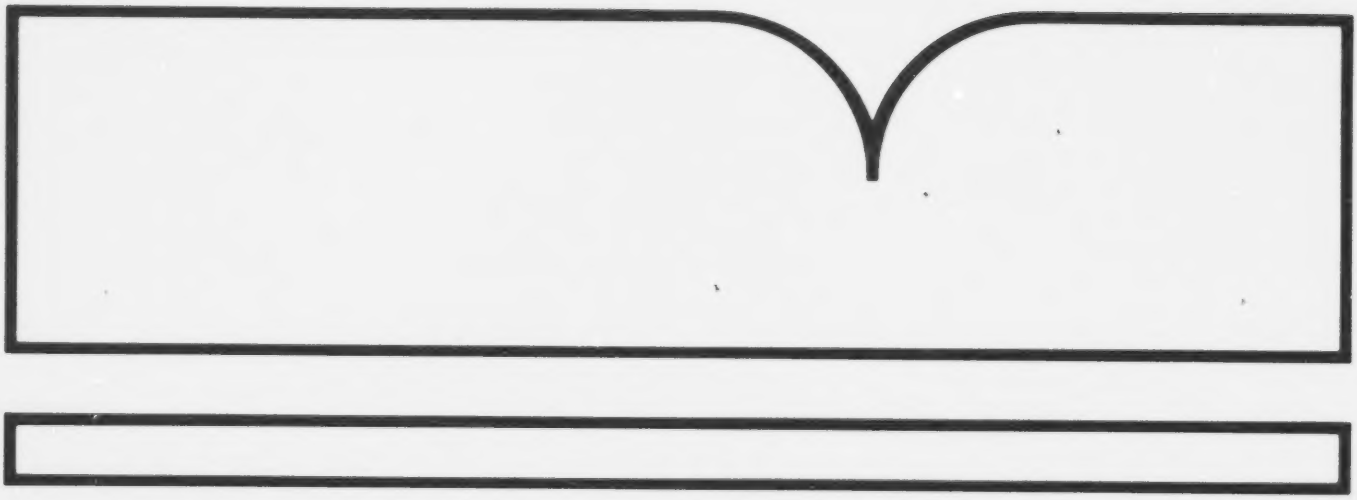

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Abstract

This report surveys currently available technologies for monitoring the operations of chemical manufacturing and handling facilities to detect airborne emissions of hazardous chemicals before they reach levels which pose an acute hazard to public health. The Survey is a first step toward providing industrial planners and plant managers with an overview of the available monitoring techniques which would aid them in designing appropriate warning and safety systems.

The Air and Energy Engineering Research Laboratory (AEERL) is concerned with accidental releases of hazardous chemicals as well as with routine emissions of air pollutants. Volatile organic compounds emitted from hazardous waste disposal sites are also of increasing concern. Chemical detection systems which are able to identify and monitor dynamic situations where hazardous materials gradually build up to dangerous levels may avert major accidents by providing timely warning to plan personnel.

Research Triangle Institute (RTI) has reviewed the literature necessary to identify typical chemicals of concern. Several organizations have constructed lists of hazardous chemicals based on various criteria. Because resources available to this project are finite, a few of the most hazardous chemicals have been selected as the basis for investigating monitoring techniques. Eventually a larger list of chemicals may be considered.

Specific instrument methods for detecting and quantifying airborne chemicals are reviewed. For each method, the results of literature review and discussions with manufacturers are presented in a uniform format. This format includes the principle of operation, physical description, suggested applications, performance data, and advantages and disadvantages. Ten methods for detecting 34 selected chemicals were examined. Research and development needs for new methods to detect these chemicals are also discussed.

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1. INTRODUCTION

1.1 PURPOSE

This report reviews currently available technologies for monitoring the operations of chemical manufacturing and handling facilities to detect airborne emissions of hazardous chemicals before they reach levels which pose an acute hazard to public health. These technologies may be quite different from those used to monitor routine concentrations of air pollutants. Accidental release detection systems should be affordable, reliable, and suitable for use by small facilities. Such systems may also be applicable to surveying process hazards in manufacturing operations.

1.2 BACKGROUND

The Air and Energy Engineering Laboratory (AEERL) is becoming more concerned with accidental releases of hazardous chemicals as well as with routine emissions of air pollutants. Recent incidents at Bhopal, India, and Institute, W.V., have sensitized the public to the potential danger of accidents in chemical manufacturing and handling facilities. Volatile organic compounds emitted from hazardous waste disposal sites are also of increasing concern. Chemical detection systems which are able to identify and monitor dynamic situations where hazardous materials gradually build up to dangerous levels may avert major accidents by providing timely warning to plant personnel. For major industrial installations, some product-specific monitoring systems have been developed. Industrial planners and plant managers, however, need a comprehensive overview of the available monitoring technology which would aid them in the design of appropriate warning and safety systems. This survey is the first step toward such an overview. Where appropriate monitoring techniques are not available, research and development needs should be identified.

1.3 APPROACH

Research Triangle Institute (RTI) has reviewed the literature to identify typical chemicals of concern. Several organizations have constructed lists of hazardous chemicals based on various criteria. These lists are discussed in section 2. Because resources available to this project are finite, a few of the most hazardous chemicals have been selected as the basis for investigating monitoring techniques. Section 3 discusses the criteria for selection of these chemicals.

RTI plans to eventually consider a larger list of chemicals. One way to generalize from a small set to a larger set is to establish a relationship between one chemical in the small set and several chemicals in the larger set. Possible relationships based on atomic, molecular, and physical properties are outlined in section 4. Monitoring techniques for the specific chemicals selected in section 3 are reviewed and compared in section 5. Research and development needs for new methods to detect these chemicals are discussed in section 6.

2. IDENTIFICATION OF POSSIBLE CHEMICALS TO BE MONITORED

Many organizations have devoted much effort in the last decade toward identifying hazardous chemicals. This effort has produced several lists of chemicals of concern under various circumstances. A report prepared by ICF, Inc., under EPA contract numbers 68-02-3976 and 68-02-4055 in December 1985 reviews the purposes of and criteria for development of hazardous chemical lists from ten domestic and international organizations. These lists are compared with the EPA's Acute Toxics List. For this project, RTI has considered the following lists of hazardous chemicals.

The Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor regulates chemicals which may be present in the workplace. Air contaminants and a listing of specifically regulated carcinogens and toxic materials are included in Subpart Z of these regulations (29 CFR 1910.1000-1046).

Permissible exposure limits for the vast majority of OSHA air contaminants are adopted from the threshold limit values (TLVs) set by the American Conference of Governmental Industrial Hygienists. These values are updated annually. Exposure limits are based on several factors, including acute or chronic toxicity, irritation, and odor. Documentation for establishing the TLV is available for each chemical assigned a TLV.

The U.S. EPA community Emergency Preparedness Program has prepared an Acute Toxics List of 403 chemicals. This list was developed as a community emergency planning guidance document. The chemicals were selected based on median or lowest lethal dose and concentration data.

By authority of Section 102 of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, EPA compiled a list of hazardous substances and reportable quantities. The CERCLA list includes hazardous substances regulated by the Clean Water Act, the Clean Air Act, and the Resource Conservation and Recovery Act.

Under authority of the N.J. Toxic Catastrophe Prevention Act, the state of New Jersey has focused on preventing the uncontrolled release of 11 toxic chemicals. The criteria for inclusion on the list are reactivity, volatility, toxicity, and volume used in N.J. This list is shown in Table 2.1.

TABLE 2.1 N.J. TOXICS LIST

NAME	STRUCTURE	CAS#
Acetylene Tetrabromide	$CHBr_2CHBr_2$	79276
Acrolein	CH_2=CHCHO	107028
Allyl Chloride	CH_2=$CHCH_2Cl$	107051
2-Aminopyridine	$C_5H_6N_2$	504290
Amitrol(e)	$C_2H_4N_4$	61825
Anisidine(o)	C_7H_9NO	90040
Anisidine(p)	C_7H_9NO	104949
Arsine	AsH_3	7784421
Benzyl Chloride	$C_6H_5CH_2Cl$	100447
bis-Chloromethyl ether	$ClCH_2COCH_2Cl$	542881
Boron tribromide	BBr_3	10294334
Boron trifluoride	BF_3	7637072
Bromacil	$C_9H_{13}BrN_2O$	314409
Bromine	Br_2	7726956
Bromine Pentafluoride	BrF_5	7789302
Bromoform	$CHBr_3$	75252
Butyl mercaptan	$C_4H_{10}S$	109795
Carbon Tetrabromide	CBr_4	558134
Chlorine	Cl_2	7782505
Chlorine Dioxide	ClO_2	10049044
Chlorine trifluoride	ClF_3	7790912
Chloroacetaldehyde	$ClCH_2CHO$	107200
∝-Chloroacetophenone	C_8H_7ClO	532274
Chloroacetyle chloride	$ClCH_2COCl$	79049
o-chlorobenzylidene Malononitrile		40915557
Chloropicrin	CCl_3NO_2	76062
Chromyl Chloride	CrO_2Cl_2	14977618
Cyanogen Chloride	CNCl	506774

Continued

TABLE 2.1 N.J. TOXICS LIST (Continued)

NAME	STRUCTURE	CAS#
Decaborane	$B_{10}H_{14}$	17702419
Diazomethane	$CH_2=N^+=N^-$	334883
Diborane	B_2H_6	19287457
Dichloroacetylene	C_2Cl_2	7572294
Dichloropropene	$ClCH_2CH=CHCl$	26952238
2,2-Dichloropropionic acid	$C_3H_4Cl_2O_2$	75990
Dichlorvos	$C_4H_7Cl_2O_4P$	62737
1,1-Dimethyl hydrazine	$(CH_3)_2NNH_2$	57147
Dimethyl Sulfate	$(CH_3)_2SO_4$	77781
Dinitrobenzene (m)	$C_6H_4N_2O_4$	99650
Dinitrobenzene (o)	$C_6H_4N_2O_4$	528290
Dinitrobenzene (p)	$C_6H_4N_2O_4$	100254
Ethyl Mercaptan	C_2H_5SH	75081
Ethylene Chlorohydrin	$ClCH_2CH_2OH$	107073
Ethyleneimine	$H_2NCH_2CH_2NH_2$	151564
Fluorine	F_2	7782414
Germanium Tetrahydride	GeH_4	7782652
Hexachlorocyclopentadiene	C_5Cl_6	77474
Hexafluoroacetone	CF_3COCF_3	684162
Hydrazine	H_2NNH_2	302012
Hydrogen Peroxide	H_2O_2	7722841
Hydrogen Selenide	H_2Se	7783075
Iodine	I_2	7553562
Iodoform	CHI_3	75478
Iron Pentacarbonyl	C_5FeO_5	13463406
Isophorone diisocyanate		4098719
Maleic anhydride	$C_4H_2O_3$	108316

Continued

TABLE 2.1 N.J. TOXICS LIST (Continued)

NAME	STRUCTURE	CAS#
N-Methyl Aniline	$C_6H_5NHCH_3$	100618
4.4-Methylene Dianiline	$CH_2\ (C_6H_4NH_2)_2$	101779
Methyl Ethyl Ketone Peroxide	Unspecified	1338234
Methyl Isocyanate	C_2H_3NO	624839
Methyl Mercaptan	CH_3SH	74931
Mevinphos	$C_7H_{13}O_6P$	7786347
Nickel Carbonyl	C_4NiO_4	13463393
Nitrobenzene	$C_6H_5NO_2$	98953
Nitroglycerin	$C_3H_5N_3O_9$	55630
Osmium tetroxide	O_sO_4	20816120
Oxygen Difluoride	OF_2	7783417
Ozone	O_3	10028156
Pentaborane	B_5H_9	19624227
Perchloromethyl Mercaptan	CCl_3SCl	594423
Phenyl Mercaptan	C_6H_5S1-1	108985
Phenylphosphine	$C_6H_5PH_2$	Unknown
Phosgene	$COCl_2$	75445
Phosphine	PH_3	7803512
Phosphorus Oxychloride	$POCl_3$	10025873
Phosphorus Pentachloride	PCl_5	10026138
Phosphorus Trichloride	PCl_3	7719122
Quinone	$C_6H_4O_2$	106514
Sodium Azide	NaN_3	26628228
Stibine	SbH_3	7803523
Sulfur Monochloride	S_2Cl_2	10025679
Sulfur Pentafluoride	S_2F_{10}	10546017
Sulfur Tetrafluoride	SF_4	7783600

Continued

TABLE 2.1 N.J. TOXICS LIST (Continued)

NAME	STRUCTURE	CAS#
Tellurium Hexafluoride	TeF_6	7783804
1,1,2,2-Tetrachloroethane	$Cl_2CHCHCl_2$	79345
TEPP (Tetraethyl Pyrophosphate)	$C_8H_{20}O_7P_2$	107493
Tetramethyl Succinonitrile	$CN\text{-}C(CH_3)_2\ C(CH_3)_2\ CN$	3333526
Tetranitromethane	$C(NO_2)_4$	509148
Toluene-2,4-diisocyanate	$C_9H_6N_2O_2$	584849
Tributyl Phosphate	$(C_4H_9)_3PO_4$	126738

The U.S. Department of Transportation (DOT) 1984 Emergency Response Guidebook lists over 3,000 hazardous materials. Of these, isolation distances are assigned for 34 hazardous materials shown in Table 2.2. Eleven of the chemicals on the N.J. Toxics List are also on the DOT Isolation Guide List: acrolein, boron trifluoride, bromine, chlorine, dimethyl sulfate, ethylenimine, fluorine, methyl mercaptan, perchloromethyl mercaptan, phosgene, phosphorus trichloride.

To narrow the scope of this project, a working list of 36 chemicals was prepared based on toxicity, production, and history of involvement in accidents resulting in death or injury. These chemicals were ranked roughly by decreasing concern. This working list, shown in Table 2.3, includes chemicals on the N.J. Toxics List as well as lists prepared for the California South Coast Air Basin and the Monsanto Chemical Co. Nine of these chemicals appeared as examples of extremely hazardous substances for review in the May 1988 EPA report to Congress, "Review of Emergency Systems."

TABLE 2.2 ISOLATION DISTANCES

NAME	STRUCTURE	CAS#	ISOLATION (ft)[a]
Acrolein	CH_2-CHCHO	107-2-8	300
Acrylonitrile	CH_2-CHCN	107-13-1	90
Ammonia, anhydrous	NH_3	7664-41-7	80
Boron trifluoride	BF_3	7637-07-2	320
Bromine	Br_2	7726-95-26	170
Carbon bisulfide	CS_2	75-15-0	50
Chloride of phosphorus	$POCl_3$	10025-87-3	110
Chlorine	Cl_2	77882-50-5	140
Dimethylamine, anhydrous	$(CH_3)_2NH$	124-40-3	80
Dimethyl sulfate	$(CH_3)_2SO_4$	77-78-1	80
Epichlorohydrin	C_3H_5ClO	106-89-8	40
Ethyleneimine	C_2H_5N	151-56-4	270
Ethylene oxide	C_2H_4O	75-21-8	80
Fluorine, cryogenic	F_2	7782-41-4	460
Hydrochloric acid, anhydrous	HCl	7647-01-0	190
Hydrocyanic acid	HCN	74-90-8	90
Hydrofluoric acid, anhydrous	HF	7664-39-3	150
Hydrogen sulfide	H_2S	7783-06-4	120
Methylamine, anhydrous	CH_3NH_2	74-89-5	110
Methyl bromide	CH_3Br	74-83-9	50
Methyl chloride	CH_3Cl	74-87-3	30
Methyl mercaptan	CH_4S	74-93-1	370
Methyl sulfate	CH_3OSO_2OH	75-93-4	80
Nitric acid	HNO_3	7697-37-2	100
Nitric oxide	NO	10102-43-9	90

Continued

TABLE 2.2 ISOLATION DISTANCES (Continued)

NAME	STRUCTURE	CAS#	ISOLATION (ft)[a]
Nitrogen dioxide	NO_2	10544-72-6	110
Oleum	H_2SO_4	8014-95-7	280
Perchloromethyl-mercaptan	CCl_3SCl	549-42-3	220
Phosgene	$COCl_2$	75-44-5	600
Phosphorous trichloride	PCl_3	77-19-12-2	110
Sulfur dioxide	SO_2	74-46-09-5	120
Sulfuric acid	H_2SO_4	7664-93-9	280
Titanium tetrachloride	$TiCl_4$	7550-45-0	30
Trimethylamine, anhydrous	$(CH_3)N$	7550-45-0	50

[a] 1 ft = 0.305 m

TABLE 2.3 WORKING LIST OF ACUTELY HAZARDOUS CHEMICALS FOR ACCIDENTAL RELEASES

Name	CAS No.	Structure	IDLH	EPA	Mons	SCAQ	NJAT	Top9	PRT1	PRT2	PR50	PHST
Chlorine	77882-50-5	Cl_2	25 ppm	X	X	X	X	X			X	G
Ammonia	7664-41-7	NH_3	500 ppm	X	X	X		X		X	X	G
Sulfuric Acid	7664-93-9	H_2SO_4	80mg/m^3	X				X		X	X	L
Hydrochloric Acid	7647-01-0	HCl	100 ppm	X			X	X		X	X	G Q
Nitric Acid	7697-37-2	HNO_3	100 ppm	X				X			X	L
Hydrogen Fluoride	7664-39-3	HF	20 ppm	X	X	X	X		X			G L
Hydrogen Cyanide	74-90-8	HCN	50 ppm	X	X	X	X		X			G L
Phosgene	75-55-5	$COCl_2$	2 ppm	X	X		X		X			G
Vinyl Chloride	75-01-4	CH_2=CHCl	NA						X	X	X	G
Benzene	100-14-1	C_6H_8	2000ppm						X	X	X	L
Styrene	100-42-5	C_8H_8	5000ppm						X	X	X	L
PCBs	*							X				L
Toluene	108-88-3	C_7H_8	2000ppm					X			X	L
Methyl Alcohol	67-56-1	CH_3OH	25,000ppm					X			X	L
Carbon Tetrachloride	56-23-5	CCl_4	300ppm			X						L
Ethylene Oxide	75-21-8	C_2H_4O	800 ppm	X							X	G
Formaldehyde	50-00-0	HCHO	100ppm	X					X		X	G O
Sulfur Dioxide	7446-09-5	SO_2	100 ppm	X		X						G
Cumene Hydroperoxide	80-15-9	$C_9H_{12}O_2$	NA							X		L
Acrylonitrile	107-13-1	CH_2=CHCN	4 ppm	X	X				X		X	L
Carbon Disulfide	75-15-0	CS_2	500 ppm	X					X			L
Bromine	7726-95-6	Br_2	10 ppm	X			X					L
Allyl Chloride	107-05-1	CH_2=CHCH$_2$Cl	300 ppm				X					L
Sodium Hydroxide	1310-73-2	NaOH	200mg/m^3					X		X	X	S
Phenol	108-95-2	C_6H_6O	100ppm	X						X	X	S

Continued

TABLE 2.3 WORKING LIST OF ACUTELY HAZARDOUS CHEMICALS FOR ACCIDENTAL RELEASES (Continued)

Name	CAS No.	Structure	IDLH	EPA	Mons	SCAQ	NJAT	Top9	PRT1	PRT2	PR50	PHST
1,2-Dichloroethane	107-06-2	$C_2H_4Cl_2$	1000ppm							X		L
Acrolein	107-02-8	$CH_2=CHCHO$	5 ppm	X	X							L
Methyl Isocyanate	624-83-9	C_2H_3NO	20 ppm	X	X		X					L
Phosphorous Trichloride	7719-12-2	PCl_3	50 ppm	X			X					L
Phosphorous	7723-14-0	P	NA	X					X			S
Toluene Diisocyanate	26471-62-5	$C_9H_6N_2O_2$	10ppm	X					X			S L
Hydrogen Sulfide	7783-06-4	H_2S	300 ppm	X	X		X					G
Chloropicrin	76-06-2	CCl_3NO_2	4ppm			X						L
Mercaptan	*				X							G
Sulfite	*				X							
Ethylene Glycol	107-21-1	$C_2H_6O_2$	80ppm							X	X	L

CAS No. - Chemical Abstract Series Number
IDLH - Concentration which is immediately dangerous to life and health
EPA - Included on EPA's Acute Toxics List
Mons - Included on Monsanto's list of chemicals of concern
SCAQ - Included on South Coast Air Basin List
NJAT - Included on New Jersey Toxics List
Top9 - One of the nine most frequent chemicals associated with accidents involving death/injury
[Acute Hazardous Events Data]
PRT1 - Annual production > 100 M Kg/yr & Tox # > 0.4 [MHAPPS2 Data]
[Modified Hazardous Air Pollutants Priority System]
PRT2 - Annual production > 1000 M Kg/yr & Tox # > 0.2 [MHAPPS2 Data]
PR50 - One of top 50 chemicals produced in 1985 [ChE News]
PHST - Physical state at standard temperature and pressure: gas, liquid, solid, Q???
* - Chemical classes
NA - Not Available

3. SELECTION OF SPECIFIC CHEMICALS

For purposes of this survey, efforts were concentrated on the acutely toxic airborne chemicals included on the EPA Acute Toxics List, the N.J. Toxics List, and the DOT Evacuation Guide List. These several hundred chemicals were ranked by acute toxicity, measured by the concentration immediately dangerous to life or health (IDLH). For chemicals with low IDLH's, additional considerations were physical state at standard temperature and pressure, appearance on multiple lists, and (where available) annual production. Information compiled from the National Library of Medicines TOXNET on-line data base, the NIOSH/OSHA "Pocket Guide to Chemical Hazards," and Chemical Engineering News included the following:

- IDLH - The concentration represents a maximum level from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.
- Boiling point at atmospheric pressure
- Vapor pressure at STP
- Appearance on EPA's Acute Toxics List, the N.J. Toxics List, or the DOT Evacuation Guide List
- Annual production quantity

Chemicals with low IDLH values are the most hazardous. From the above-mentioned lists, RTI selected those chemicals with IDLH ≤ 5 ppm (15 chemicals), those with $5 <$ IDLH ≤ 10 ppm (15 chemicals), and for aerosols, those with IDLH < 3 mg/m^3 (6 chemicals). These 36 chemicals are shown in Tables 3.1, 3.2, and 3.3, respectively.

These chemicals were compared with those on the working list of 36 acutely hazardous chemicals. Most of the chemicals on the working list have IDLH values > 10 ppm. Seven chemicals appear on both lists: phosgene, acrylonitrile, bromine, acrolein, methyl isocyanate, toluene diisocyanate, and chloropicrin. RTI initially looked at monitoring techniques for these seven chemicals. At EPA's request, RTI then searched for monitoring techniques for seven additional inorganic chemicals: chlorine, ammonia, sulphuric acid, hydrochloric acid, nitric acid, hydrogen fluoride, and hydrogen cyanide. Ten monitoring techniques were identified for these fourteen chemicals. Many of these techniques could be used for other chemicals as well. Eventually RTI tabulated the applicability of these ten methods for all the chemicals in the working list.

TABLE 3.1 CRITERIA FOR SELECTION OF TOXIC CHEMICALS WITH IDLH ≤ 5 PPM
FOR THE SURVEY OF INDUSTRIAL HAZARD ANTICIPATION TECHNOLOGY

IDLH ≤ 5 ppm	BP ≤ 25°C	VAP PRESS ≥ 100 mm Hg STP	EPA ATCL	NJ LIST	DOT EVAC. GUIDE	DOT POISON	> b#/yr	> 1m#/yr
Acrolein	No	Yes	Yes	Yes	Yes	Yes	No	Yes
Acrylonitrile	No	Yes	Yes	No	Yes	Yes	Yes	Yes
Phosgene	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
2-Aminopyridine	No	-	No	Yes	No	No	ND	ND
Chloropicrin	No	No	No	Yes	No	Yes	No	Yes
Hydrogen Selenide	Yes	Yes	Yes	Yes	No	Yes	ND	ND
Monomethyl Hydrazine	No	No	Yes	No	No	Yes	No	No
Nickel Carbonyl	No	Yes	Yes	Yes	No	Yes	ND	ND
Oxygen Difluoride	Yes	Yes	No	Yes	No	No	ND	ND
Pentaborane	No	Yes	Yes	Yes	No	Yes	ND	ND
Selenium Hexafluoride	Yes	Yes	No	No	No	No	ND	ND
Sulfur Pentafluoride	No	Yes	No	Yes	No	No	ND	ND
Tellurium Hexafluoride	Yes	Yes	Yes	Yes	No	No	ND	ND
Tetramethyl Succinonitrile	No	?	No	Yes	No	No	ND	ND
Tetranitromethane	No	No	Yes	Yes	No	No	No	No

IDLH Level = Immediately Dangerous to Life or Health Criteria (NIOSM)
BP = Boiling Point
VAP Press = Vapor Pressure in mm of Hg
ATCL = Acutely Toxic Chemicals List - Mammalian Testing (EPA)
NJ List = New Jersey List Criteria of TLV less than 1 ppm and reactive compound (NJ/EPA)
DOT Evac. Guide = Used for isolating and evacuating unprotected people from spill areas (DOT)
DOT Poison = Poisonous Substances List (DOT)
b#/yr = Production of 1 billion pounds per year or more (1 pound = 454 g)
1m#/yr = Production between 1 million and 1 billion pounds per year

TABLE 3.2. CRITERIA FOR SELECTION OF TOXIC CHEMICALS WITH IDLH FROM 5.1 TO ≤ 10 PPM FOR THE SURVEY OF INDUSTRIAL HAZARD ANTICIPATION TECHNOLOGY

IDLH 5.1 to ≤ 10 ppm	BP ≤ 25°C	VAP PRESS ≥ 100 mm Hg STP	EPA ATCL	NJ LIST	DOT EVAC. GUIDE	DOT POISON	> b#/yr	> 1m#/yr
Bromine	No	Yes	Yes	Yes	Yes	No	No	Yes
Dimethyl Sulfate	No	No	Yes	Yes	Yes	No	No	No
Perchloromethyl mercaptan	No	No	Yes	Yes	Yes	Yes	ND	ND
Toluene diisocyanate	No	No	Yes	Yes	No	Yes	ND	ND
Acetylene tetrabromide (1,1,2,2 - Tetrabromoethane)	No	No	No	Yes	No	No	No	No
Arsine	Yes	Yes	Yes	Yes	No	Yes	No	No
Benzyl Chloride	No	No	Yes	Yes	No	No	No	Yes
Chlorine Dioxide	Yes	Yes	No	Yes	No	No	ND	ND
Diazomethane	Yes	Yes	No	Yes	No	No	ND	ND
Dimethylsulfate	No	No	Yes	Yes	Yes	No	No	No
Ethylene Chlorohydrin	No	No	Yes	No	No	Yes	No	Yes
Iodine	No	No	No	Yes	No	No	No	No
Methylene biphenyl isocyanate	No	No	No	No	No	No	No	Yes
Ozone	Yes	Yes	No	Yes	No	No	No	Yes
Sulfur chloride	No	No	No	Yes	No	No	ND	ND

IDLH Level = Immediately Dangerous to Life or Health Criteria (NIOSM)
BP = Boiling Point
VAP Press = Vapor Pressure in mm of Hg
ATCL = Acutely Toxic Chemicals List - Mammalian Testing (EPA)
NJ List = New Jersey List Criteria of TLV less than 1 ppm and reactive compound (NJ/EPA)
DOT Evac. Guide = Used for isolating and evacuating unprotected people from spill areas (DOT)
DOT Poison = Poisonous Substances List (DOT)
b#/yr = Production of 1 billion pounds per year or more (1 pound = 454 g)
1m#/yr = Production between 1 million and 1 billion pounds per year

TABLE 3.3. CRITERIA FOR SELECTION OF TOXIC CHEMICALS WITH IDLH $\leq$ 3 mg/m^3 FOR THE SURVEY OF INDUSTRIAL HAZARD ANTICIPATION TECHNOLOGY

IDLH $\leq$ 3mg/m^3	BP $\leq$ 25°C	VAP PRESS $\geq$ 100 mm Hg STP	EPA ATCL	NJ LIST	DOT EVAC. GUIDE	DOT POISON	> b#/yr	> 1m#/yr
Osmium tetroxide	No	No	Yes	Yes	No	No	No	No
Paraquat	No	No	Yes	No	No	No	ND	ND
Pentaborane	No	Yes	Yes	Yes	No	Yes	ND	ND
Strychnine	No	No	Yes	No	No	Yes	ND	ND
O-Chlorobenzylidene malonitrile	No	No	No	Yes	No	No	ND	ND
Hexachloronaphthalene	No	No	Yes	No	No	No	ND	ND

IDLH Level = Immediately Dangerous to Life or Health Criteria (NIOSM)
BP = Boiling Point
VAP Press = Vapor Pressure in mm of Hg
ATCL = Acutely Toxic Chemicals List - Mammalian Testing (EPA)
NJ List = New Jersey List Criteria of TLV less than 1 ppm and reactive compound (NJ/EPA)
DOT Evac. Guide = Used for isolating and evacuating unprotected people from spill areas (DOT)
DOT Poison = Poisonous Substances List (DOT)
b#/yr = Production of 1 billion pounds per year or more (1 pound = 454 g)
1m#/yr = Production between 1 million and 1 billion pounds per year

4. CLASSIFICATION OF CHEMICALS FOR SENSOR/MONITOR IDENTIFICATION

Table 4.1 lists the chemicals of concern and their class, IDLH (immediately dangerous to life or health), and structure. Monitors appropriate for each class have been sought. Techniques appropriate for a class of chemicals and which may be tuned for specific chemicals in that class have also been sought. Section 5 discusses examples of some of the techniques.

TABLE 4.1. CHEMICALS OF CONCERN

Chemical Name	Class	IDLH, ppm	Structure
Acrolein	Aldehydes	5	CH_2=CHCHO
Acrylonitrile	Nitriles	4	CH_2=CHCN
Phosgene	chlorides	2	$COCl_2$
Chloropicrin	chlorides	4	CCl_3NO_2
Bromine	Inorganic/Halogen	10	Br_2
Methyl Isocyanate	Isocyanate	20	C_2H_3NO
Toluene Diisocyanate	Isocyanate	10	$C_6H_6N_2O_2$
Chlorine	Inorganic	25	Cl_2
Ammonia	Inorganic	500	NH_3
Sulfuric Acid	Inorganic	80 mg/m3	H_2SO_4
Hydrochloric Acid	Inorganic	100	HCl
Nitric Acid	Inorganic	100	HNO_3
Hydrogen Fluoride	Inorganic	20	HF
Hydrogen Cyanide	Inorganic	50	HCN
Vinyl Chloride	Chlorides	NA	CH_2 = CHCl
Benzene	Organic	2000	C_6H_6
Styrene	Organic	5000	C_6H_5CH = CH_2
Toluene	Organic	2000	$C_6H_5CH_3$
Carbon Tetrachloride	Chlorides	300	CCl_4
Ethylene Oxide	Organic	800	C_2H_4O
Formaldehyde	Aldehyde	100	HCHO
Sulfur Dioxide	Inorganic	100	SO_2
Cumene Hydroperoxide	Organic	NA	$C_9H_{12}O_2$
Carbon Disulfide	Organic	500	CS_2
Allyl Chloride	Chloride	300	Ch_2 = $CHCH_2$ Cl
Chloroform	Organic	1000	$CHCl_3$
Tetraethyl Lead	Organic	40 mg/m^3	$Pb(C_2H_6)_4$

Continued

TABLE 4.1. CHEMICALS OF CONCERN (Continued)

Chemical Name	Class	IDLH, ppm	Structure
Phenol	Organic	100	C_6H_6O
1,2-Dichloroethane	Organic	1000	$C_2H_4Cl_2$
Phosphorus Trichloride	Chlorides	50	PCl_3
Phosphorus	Inorganic	NA	P
Mercaptans	Mercaptans	*	*
Sulfites	Sulfites	*	*
Ethylene Glycol	Organic	80	$C_2H_6O_2$

* - Chemical Classes

NA - Not Available

5. IDENTIFICATION OF EXISTING SENSOR/MONITOR TECHNIQUES

This section reviews specific instrument methods for detecting and quantifying airborne hazards. The following outline details each subsection. Most of the information in this section was collected from instrument manufacturers and promotional literature.

Table 5.1 is a matrix of chemicals to be measured vs. measurement methods. Table 5.2 is a summary of specifications, as provided by the instrument manufacturers.

References appear beside the method of detection. References (1) and (2) are general sources of information. References (3) to (18) are manufacturers that provided literature concerning a specific product(s).

5.X METHOD OF DETECTION

This section gives a description of where information was collected. The specific instruments investigated are listed.

5.X.1 Principle of Operation

The basic technique of detection is explained.

5.X.2 Physical Descriptions and Applications

The subsection includes size, weight, available accessories, power requirements, alarm options and the manufacturers suggestions for application.

5.X.3 Performance Data

The sensitivity, range, accuracy and chemicals that can be detected are listed.

5.X.4 Advantages

5.X.5 Disadvantages

TABLE 5.1 MATRIX OF CHEMICALS VS. METHODS

Chemicals	Colorimetric Tape	Continuous Colorimetric	Derivative Spec	IR Spec	Fourier Spec	Laser System	GC/PID	MS	Halide	Diffusion/ Electrochem.
Acrolein				X	X	X	X	X		
Acrylonitrile				X			X	X		
Phosgene	X			X	X	X	X			X
Chloropicrin				X						
Bromine		X							X	X
Methyl Isocyanate				X						
Toluene Diisocyanate	X				X			X		
Chlorine		X						X	X	X
Ammonia		X		X	X	X	X	X		X
Sulfuric Acid/H_2S	X	X		X	X		X	X		X
Hydrochloric Acid		X		X	X			X		X
Nitric Acid								X		
Hydrogen Fluoride		X		X	X			X		X
Hydrogen Cyanide		X		X	X		X	X		X
Vinyl Chloride				X	X	X	X	X		
Benzene				X		X	X	X		
Styrene				X		X	X	X		

Continued

TABLE 5.1 MATRIX OF CHEMICALS VS. METHODS (Continued)

Chemicals	Colorimetric Tape	Continuous Colorimetric	Derivative Spec	IR Spec	Fourier Spec	Laser System	GC/PID	MS	Halide	Diffusion/ Electrochem.
Toluene				X	X		X	X		
Carbon Tetrachloride				X			X	X	X	
Ethylene Oxide				X		X	X	X		
Formaldehyde		X		X	X		X			
Sulfur Dioxide				X	X			X		X
*Cumene Hydroperoxide										
Carbon Disulfide				X	X		X	X		
Allyl Chloride				X	X		X	X		
Phenol		X		X	X		X	X		
1,2-Dichloroethane						X	X			
Phosphorus Trichloride										X
*Phosphorus										
Mercaptans		X					X			
*Sulfites										
Ethylene Glycol		X					X	X		
Chloroform							X			
Tetraethyl Lead							X	X		

*no measurement method found

TABLE 5.2 SPECIFICATIONS OF MONITORING TECHNIQUES

	Sensitivity/Range	Accuracy	Response Time	Power Requirements	Size[a]	Weight	Alarm Options	Cost
Colorimetric tape	0-20 ppb 0-200 ppb option	±15% of reading or ±1 ppb, whichever is greater	user set 24 or 240 seconds	115 V, 60 Hz	10" x 5" x 4"	5.4 lbs.	audible, visual	$1,995
Continuous Colorimetric	C/2 0-2 ppm/0.002 ppm fullscale ±3% precision	1% reproducibility	1-8 minutes	120 VAC, 60 Hz	20" x 16" x 7"	30 lbs.	audible, visual	$5,495
Derivative Spec	ppb	NA	user set 1, 3, or 10 seconds	115 VAC ±10% Hz, 150 watts	24" x 20" x 15"	132 lbs.	NA	$30-40,000
IR Spec	IR spectral range 2.5 to 14.5 micrometers acrolein 0.9ppm	±5% of reading	15 seconds	120 V, 60 Hz	18" x 6" x 8"	18 to 32 lbs.	audible, visual, automatic	NA
Fourier Spec	Acrolein: 0.008 ppm	Photometric Accuracy: 0.1% to 100% transmittance	NA	NA	NA	NA	NA	NA
Laser System	1 to 400 ppm-m (typical)	better than 5%	< 1 second	110 V/60 Hz, single phase < 20A	42" x 44" x 28"	300 lbs.	audible, visual, automatic	$170,000
Gas Chromatograph Photoionization Detector (GC/PID)	0-20, 0-200, 0-2000 ppm PID sensitivity 1-50ppb	0.1 ppb: PID	< 3 seconds	115 VAC, 60 Hz GC/110 VAC PID	GC 6" x 9" x 15" PID 11" x 16" x 9"	Portable GC 15-40 lbs. PID 3-10 lbs.	audible, visual, plus automatic for multipoint GC	$3-5,000 GC $4,000 PID
MS	ppt/TDI 10 ppb	systems noise < 10 ions/second	as low as 0.5 seconds	500 watts	monitor 22" x 31" x 22" analyzer 9" x 31" x 22"	130-160 lbs.	NA	NA
Halide	±3% precision	±5% accuracy	3-5 seconds	20V, 50/60 Hz	11" x 7" x 7"	13 lbs.	NA	NA
Diffusion/ electrochem.	C/2 0-3 ppm	< ±10% full scale	10-15 seconds	15-30 VDC	8.5" x 4.3" x 6.8"	3.4 lbs.	audible, visual	NA

NA = not available

[a] 1 inch = 2.54 cm

5.1 COLORIMETRIC PAPER TAPE MONITOR (3)

5.1.1 Principle of Operation

A specific colorimetric reactive system is impregnated into paper tape contained in a removable cassette system. In operation, a pump pulls a controlled sample of the atmosphere through the tape, causing a color to be developed if the specific gas is present. The tape is continuously monitored by a light emitting diode/photodiode combination which translates color intensity to a readout on the first of two bargraph liquid crystal displays. After a predetermined interval, the tape is incremented forward and the next sample is taken. At the start of each test, a reading is taken of the background color of the tape which is stored in a memory system and then subtracted from the reading at the end of the sampling period to yield the actual change in tape color during the sampling interval.

5.1.2 Physical Description and Applications

The monitor is 10" x 5" x 4" and weighs 5.4 pounds. The power requirement is 115V, 60Hz. Battery operation is available for up to 36 hours depending on operation mode. The case is made of impact-resistant polycarbonate, with sealed lid and stainless steel catches. Three different operating modes are available, each having a different combination of pump sampling rate and sampling interval designed to suit a different application in detection and control of a specific gas. The three modes are as follows:

1) Search - Leak detector, fast response with extended range

2) Survey - Portable monitor for atmospheric checking, 1ppb sensitivity

3) Monitor - area monitoring with maximum tape and battery conservation.

When used with the recorder module, the monitor becomes a complete portable area monitoring system, completely weatherproof for use in typical plant locations under adverse conditions. Audible and visual alarm options are available from the manufacturer.

5.1.3 Performance Data

The first column of the dual-column bargraph display is used to show the immediate value of stain color with an actual ppb readout at the end of the sampling interval. A special override circuit causes the tape to advance automatically in the event of a high concentration being detected, giving a rapidly moving display under these conditions. Dual ranges of 0-20 ppb or 0-200 ppb isocyanates are available with an accuracy of ± 15% of the reading or ± 1 ppb, whichever is greater. Specific gases from Table 4.1 that can be monitored include isocyante, phosgene, and hydrogen sulfide. Similar monitors are available for hydrazines.

5.1.4 Advantages

- Portable (can be battery-powered)
- Inexpensive ($1995)
- Easy to operate
- No warm-up time or instrument drift
- Highly reliable solid-state monitoring optics

5.1.5 Disadvantages

- Not automation/computer-compatible
- Capability limited to monitoring one gas at a time

5.2 CONTINUOUS COLORIMETRIC ANALYZER (1, 4, 3)

5.2.1 Principle of Operation

An air sample is continuously drawn into the unit and scrubbed with an absorbing reagent which removes a trace pollutant from the air stream and transfers it into the liquid reagent system.

The subsequent color formation is read by a colorimeter and displayed on a digital readout. A recorder output is also provided.

5.2.2 Physical Description and Applications

The Instrument is 20" x 16" x 7" in size and weighs 30 pounds. The power requirements are twelve VDC unregulated, 310 mA, 4 watts (external 10.2 VDC minimum) 120 VAC, 60 Hz, 35 watts maximum. The instrument can operate 12 hours on fully charged internal batteries. Available accessories include reactor chamber, heating bath, stream splitter, and chart recorder. The signal output is 0-1.0 V at 0-2.0 mA. It was designed to be hand carried into the field, into the plant, as well as used in stationary installation and moving vehicles. Audible and visual alarm options are available through manufacturer.

5.2.3 Performance Data

The following performance data is for Cl_2. The operating range is 0-2 ppm full scale, adjustable up to 0-5 ppm. Reproducibility is 1%. Drift is < 2% in 24 hours. The minimum detectable concentration is 0.002 ppm full scale. Measurement of chemicals from Table 4.1 include NH_3, TDI, HCN, acrylonitrile, bromine, Cl_2, hydrogen chloride, and hydrogen sulfide. Continuous colorimetric analysis of SO_2, NO_2, NO_x, HCHO, fluorine, hydrazine, or total oxidants can also be done.

5.2.4 Advantages

- Easy to operate
- Portable (battery operated)
- Low cost ($5,495)

5.2.5 Disadvantages

- Reagent required
- Slower response than some instruments (1-8 minutes)

5.3 DERIVATIVE SPECTROSCOPY (1, 2, 5)

5.3.1 Principle of Operation

In derivative spectroscopy, the first or n^{th} derivative of the transmission versus wavelength function of an ordinary spectrometer is processed into a signal proportional to the wavelength. The derivative signal considerably enhances the ability to detect overlapping spectral lines and bands. Fluctuating light source effects are suppressed. The detection and measurement of minor spectral differences such as the signal-to-noise ratio, the resolution of the data, and the sensitivity are greatly improved. Characteristic spectral detail can be distinguished from similar spectra and subtle changes in a spectrum can be followed because derivative spectroscopy is concerned with the shape characteristics rather than with the basic intensity changes, or spectral distribution. The slope and curvature characteristics are often quite large, very specific and largely independent of intensity. These shape characteristics are large, yet specific to individual compounds, allowing derivative spectroscopy to be used in quantitative analysis to measure the concentration of an analyte whose peak is obscured by a larger overlapping peak due to an interference. This enables the elimination of prior separations. The derivative spectra may be recorded in real time either by wavelength modulation or by obtaining the time derivative of the spectrum scanned at a constant rate using a simple differentiator.

5.3.2 Physical Description and Applications

The control unit is 24" x 20" x 15" and the sample cell unit is 9" x 58" x 24"; together, their weight is 132 pounds. Sample flow through the cell may be continuous (analysis independent of sample rate), or may be stopped to continuously analyze a fixed sample. Two standard forward scan speeds are provided. "Dwell" mode operation is available for continuous, single-component analysis. Instrument output to an analog chart recorder may be switch-selected to provide either the second-derivative spectrum (the compound is identified by the peak location, and the concentration is measured by peak height) or a direct absorption. No information concerning power requirements, alarm options or applications was disclosed by the manufacturer.

5.3.3 Performance Data

Derivative spectroscopy is capable of identifying any compound which exhibits narrow-band absorption of ultraviolet or visible radiation. It is capable of continuously monitoring a single compound. A partial list of compounds from Table 4.1 which can be identified and measured by derivative spectroscopy is: acrolein, ammonia, and chlorine. Acetaldehyde, acetylene, aniline, benzaldehyde, benzene, benzene in water, bromobenzene, 2,3-butanedione, carbon disulfide, methylamine, ethylbenzene, formaldehyde, furfural, glyoxal iodine, isopropylbenzene, metaxylene, naphthalene, nitrogen dioxide, nitric oxide, nitrobenzene, orthobromoaniline, orthochlorobenzene, orthoxylene, oxygen, ozone, paradichlorobenzene, paraxylene, pest strip, phenol, pyrrodiline, pyridine, styrene, sulfur dioxide, titanium, tetrachloride, toluene, and unsymmetrical dimethydrazine can also be measured.

Low end detection extends down to the ppb concentration levels and there is essentially no upper limit to the concentrations which can be detected. Where concentrations are so high that an unusually large portion of the light radiation is absorbed, the pathlength through the sample can be reduced to prevent total light absorption.

Molecular band absorption and curvature of individual bands are unique properties. This provides the key to the high interference-rejection capabilities of derivative spectroscopy. In order to interfere with a measurement, a compound must exhibit narrow-band absorption, creating curvature in the intensity distribution at the identical wavelength and of the same magnitude as the compound of interest. Such stringent requirements for an interferent insure a highly specific measurement in the most complex gas mixtures.

The wavelength is displayed on the front panel in angstroms (A). The standard wavelength range is 2000 A to 6000 A. A section of ultraviolet or visible light is manual from the front panel. Two standard forward scan speeds are selectable from the front panel: 25 A/minute and 100 A/minute. "Dwell" mode operation is available for continuous, single-component analysis. Four time constants are switch-selectable from the front panel: 1, 3, 10 or 30 seconds. Four attenuation ranges are switch selectable from the front panel: 0.33, 1.0, 3.3, or 10. The resolution is 4 A with the standard 100-micron slit width. Both 25- and 50-micron slit widths are also available.

5.3.4 Advantages

- Quick response
- Variety of gases detectable
- Interferences unlikely
- Wide concentration range/very sensitive
- No sample alteration or conditioning before analysis
- Portable models available

5.3.5 Disadvantages

- Cost
- Complex

5.4 INFRARED SPECTROMETER (6)

5.4.1 Principle of Operation

Infrared (IR) energy is emitted from a nichrome wire source through a light pipe assembly. The light is then directed to a filter wheel that allows energy at a selected wavelength to pass through into a gas cell. The sample is drawn into the cell by an integral air pump at a rate of 25 to 30 litres per minute (L/min). The sample adsorbs infrared energy from the beam and the amount of absorption is measured by the detector, amplified and converted to concentration units by the electronics, and transmitted to a liquid crystal display. The amount of infrared radiation adsorbed by a sample is directly related to the concentration.

5.4.2 Physical Description and Applications

IR spectrometers are available as portable or multipoint (stationary) instruments.

Portable IR spectrometers vary in size from 18.5" x 5.9" x 7.5" to 27.8" x 9" x 11" and in weight from 18 to 32 pounds. The models investigated were of two basic set-ups, either a fixed IR filter allowing only one gas to be measured or an unfixed IR filter that allows scanning capabilities. All models can be battery operated for four hours. Accessories include spectra books, chart

recorder, heating jack and temperature controller, closed loop calibration system and zero gas purging system. A dual set-point audible and visual alarm is an option on most models and standard on one model. Applications discussed by the manufacturer include:

- Industrial Hygiene Measurements for OSHA Compliance
- Hospital and Pharmaceutical
- Semi-conductor Manufacturing
- Chemical Plants
- Petrochemical Facilities
- Textile Manufacturing
- Process Analysis

The multipoint models are approximately 70" x 65" x 70" and weigh 350 pounds. They also have two set-ups available, either single or multicomponent monitoring. The multipoint systems allow monitoring at up to 24 remote locations, up to 984 feet from the analyzer. Optional features include interconnecting cable, closed-loop calibration system, zero gas filter assembly, nitrogen gas regulator, cell heater jacket and temperature controller, single component compensation, dual component compensation. Two alarm options are available, single-or dual-level remote alarm relays. Internal relays are provided for each sample point monitored. These relays can be used to actuate alarms at the corresponding remote point to warn personnel of approaching safe exposure limits.

Applications discussed by the manufacturer include:

- Employee exposure monitoring
- Chemical leak detection
- Control of ventilation systems
- Perimeter monitoring

5.4.3 Performance Data

The portable IR spectrometers have an accuracy of ± 5% of the reading. Response time is 15 seconds average. These analyzers are equipped with a circular variable filter which covers the IR spectral range of 2.5 to 14.5 micrometers. Some gases from Table 4.1 included in this range and the detection are

limits are acrolein 0.9 ppm, acrylonitrile 0.6 ppm, phosgene 0.1 ppm, chloropicrin 0.1 ppm, methyl isocycanate 0.1 ppm, ammonia 0.5 ppm, hydrogen fluoride 10.0 ppm, hydrogen cyanide 1.7 ppm, hydrogen chloride 4.8 ppm, and hydrogen sulfide 270 ppm.

The multipoint IR spectrometers have an absorbance range of 0.0 to 3.5 absorbance units printed in increments of 0.0001 absorbance units. The wavelength repeatability at 0.5 mm slit width is ± 0.0004 µm at 2.5 to 4.5 µm wavelength, ± 0.0008 µm at 4.4 to 8.0 µm wavelength and ± 0.0014 µm at 7.9 to 14.5 µm wavelength. Resolution at the 0.5 mm slit width is 0.05 µm at 3.5 µm wavelength, 0.08 µm at 6 µm wavelength, and 0.22 µm at 12 µm wavelength. Available slit settings are 0.5 mm, 1 mm, 2 mm, and closed these are manually selectable. The IR filters have the same range and capabilities as the portable models.

5.4.4 Advantages

- Portable models available
  - Easy operation with direct readout
- Audible and visual alarms available
- Scanning capability on some models
- Multipoint models available
  - Can monitor up to 24 remote locations
  - Sample points can be up to 1000 feet away
  - Does not require carrier gases

5.4.5 Disadvantages

- Warm-up time (60 minutes)

5.5 FOURIER INTERFEROMETRY-SPECTROMETRY (1, 2, 7)

5.5.1 Principle of Operation

Interferometer-spectrometer is a dispersive-type instrument that permits an examination of a large portion of the spectrum, which eventually can be displayed as a function of wavelength. After passing through a sample, the infrared radiation is analyzed by a scanning Michelson interferometer instead of a monochromater as in infrared spectroscopy. Interferometry first generates a

frequency spectrum signal by light interference in an optical system. This signal is known as an interferogram. The frequency spectrum is converted by a mathematical process known as Fourier transformation into the conventional wavelength spectrum. A conventional scanning dispersive spectrometer generates a spectrum by serially scanning the spatially disperse wavelengths as a function of time. The interferometer has the multiplexing capability, whereby all the wavelengths are scanned concurrently in time and are measured directly as a frequency spectrum. Because all wavelengths are detected through the scan, the scanning interferometer achieves the same spectral signal-to-noise ratio as a dispersive spectrometer in a fraction of the time.

5.5.2 Physical Description and Applications

No physical description available. No alarm options described by the manufacturer. Applications according to a manufacturer include the following:

- Automated gas monitoring system
- Process control system
- Prime sensor for safety standard monitoring

5.5.3 Performance Data

Resolution is better than 0.06 cm^{-1} (continuously variable from 0.06 cm^{-1} to 8 cm^{-1}). The HeNe laser interferometer insures a frequency accuracy of better than 0.01 cm^{-1} at 4000 cm^{-1}. Photometric accuracy is better than 0.1% to 100% transmittance. Detectable gases from Table 4.1 include Acrolein at 0.008 ppm, Ammonia at 0.020 ppm, Hydrogen chloride at 0.05 ppm, Hydrogen fluoride at 0.09 ppm, Hydrogen Cyanide at 0.05 ppm, Hydrogen sulfide at 2.4 ppm Phosgene at 0.03 ppm and Toluene -2,4,-Diisocyanate at 0.008 ppm. The above sensitivities are quoted for 15 to 45 second typical measurement time. Initial studies by the manufacturer indicate that the Fourier spectrometer is able to monitor all gases presently regulated by OSHA as well as most of those regulated by EPA. The manufacturer claims the instrument is capable of making sensitive measurements without interference from other gases that may be in the work atmosphere. Interferometer-spectrometers can monitor five (5) or more gases simultaneously.

5.5.4 Advantages

- Very sensitive
- Measures variety of classes of chemicals
- Measures 5 or more gases simultaneously
- Dispersion or filtering is not required

5.5.5 Disadvantages

- Involved operational procedure, adding to the complexity and cost of the instrumentation
- No alarm options available through manufacturer

5.6 LASER SYSTEM (8)

5.6.1 Principle of Operation

Laser remote sensing systems are based upon a technique known as DIAL (Differential Absorption LIDAR). LIDAR is an acronym for Light Detection and Ranging.

The DIAL technique is based on the fact that each gas has a unique infrared absorption spectrum. A laser with a wavelength coincident with the gas under investigation transverses the monitoring area. The beam is then returned to the laser system and its signal level measured. The difference in the return signal as opposed to the output signal gives a precise measurement of the amount and concentration of gas present. Changes in the environment due to weather and objects are taken into account by using a second laser whose wavelength is not absorbed by the gas. These two laser wavelengths are chosen so that atmospheric absorption and scattering are the same for each, thus eliminating the differences due to atmospheric pressure, temperature, and humidity on output signals.

5.6.2 Physical Description and Applications

The laser unit is 42" x 44" x 28" and weighs approximately 300 pounds. The manufacturer claims that the laser system has the capability of remotely sensing the presence of hazardous gases at ranges of up to 200 meters in a continuous scanning mode and more than 5 kilometers in a pulsed or line-of-sight mode.

Some applications listed by the manufacturer include the following:

- Chemical plant and petroleum refinery scanning
- Off-shore drilling platform surveillance
- Oil and gas pipeline leak detection
- Environmental surveys
- Perimeter monitoring
- Hazardous waste disposal site surveillance
- Storage tank area scanning

Due to rapid response of the laser receiver, alarms can be activated within seconds of the detection of danger levels. Laser systems may also be linked to existing computer systems. Laser systems can detect a variety of gases depending on the type of laser used in the system.

5.6.3 Performance Data

The actual number calculated by the DIAL algorithm is total gas column content along the beam, measured in parts per million-meter (ppm-m). For example, a reading of 10ppm-m represents a gas column of one meter with a concentration of 10ppm or a length of 10 meters and a concentration of 1ppm. The sensitivity is gas-dependent, but generally 1ppm-m is the lower limit. The manufacturer claims accuracy of typically better than 5%. The following gases from Table 4.1 are suitable for monitoring with a CO_2 laser: acetonitrile, acrolein, ammonia, and phosgene. Other gases suitable for monitoring include: benzene, butadiene, t-Butanol, butene, chloroethylene, chloroprene, cyclohexane, 1,2-dichloroethane, ethyl acrylate, ethyl mercaptan, ethylene, ethylene oxide, freon 11, 12, 113, furan, iodopropane, iso-propanol, methanol, methyl chloroform, methyl ethyl ketone, methyl mercaptan, monochloroethane, ozone, perchloroethylene, propane, i-propanol, propylene, stylene, tetrachloroethylene, vinyl chloride, and water.

5.6.4 Advantages

- Quick response (less than 1 second in most cases)
- Variety of alarm options
- Variety of gases detectable
- Versatile system
- Self-calibrated and self-monitoring system
- Interferences unlikely
- Low maintenance

5.6.5 Disadvantages

- Cost ($170,000)
- Complex to setup and move

5.7 GAS CHROMATOGRAPHY/PHOTOIONIZATION DETECTOR AND ANALYZER (1, 2, 9, 10, 11, 12)

5.7.1 Principle of Operation

Gas Chromatography (GC) is primarily a method of resolving complex mixtures, and this depends on the differential migration of the components through a porous medium. This differential migration is carried out so that each component separates as a discrete substance. The separated substances appear in a carrier gas as a function of time as the carrier gas passes through the absorption column. Each substance will travel at its own rate through the column. The substances exit the column sequentially and enter a detector. If a recorder is used, the signals appear on a chart as a plot of time versus composition. The time emergence of a peak is characteristic for each component; the peak area is proportional to the concentration of the component in the original sample. GC alone does not serve directly for the detection of substances; nor does it provide an estimate in the absolute sense. As an analytical system, gas chromatography utilizes various sensitive detection techniques.

Photoionization is the process of absorption of ultraviolet (UV) light by a molecule which leads to ionization.

The sensor consists of a sealed ultraviolet light source that omits photons which are energetic enough to ionize many trace species (particularly organics) but do not ionize the major components of air such as O_2, N_2, CO, CO_2, or H_2O. A chamber adjacent to the ultraviolet source contains a pair of electrodes. A positive potential applied to the accelerating electrode creates a field which drives ions formed by adsorption of the UV light to the collecting electrode where the current (proportional to concentration) is measured.

5.7.2 Physical Description and Applications

A typical portable automatic GC weighs from 15 to 40 pounds and is approximately 6" X 9" x 15" in size. Portable automatic GCs can be used to automatically sample ambient air or used manually to handle injections. In the example models investigated, battery operation is designed to last for eight hours.

An example multipoint sampling GC (stationary) weighs 145 pounds and is 34" x 18" x 24" in size. Multipoint samplers typically consist of 10 three-way valves controlled by a microprocessor so that one sample at a time is switched to the sampling manifold while others are vented to the exhaust pump. Sample is flowing continually through the sampling lines so that it is immediately available when valves are switched. Applications for portable automatic GCs and multipoint sampling GCs are dependent upon the detector used. Most all organic vapors can be determined using a GC and a detector. Alarm options available from the manufacturers for the example GCs include audible and visual for the portable models plus automated for the multipoint model.

The photoionization detector is designed for installation into a gas chromatograph. The detector option contains its own high voltage source for the operation of the photoionization lamp. The system has several valve options available. The heated photoionization detector may be utilized in the analysis of a variety of materials. A certain degree of energy selectability is possible by interchanging photoionization lamps (lamp energies from 10.0 to 11.8 eV are available). One photoionization instrument investigated consists of two separate units; sensor and readout connected by a three foot shielded multi-conductor cable with electrical connector. The readout measures 11" x 5 1/4" x 8 1/4", weighing less than 8 pounds. The sensor measures 10" long and 2 1/2"

maximum diameter and weighs 20 oz. The readout has the following on its front panel: battery check; stand by; 0-2000, 0-200, 0-20 ranges; 10 turn counting span potentiometer; and one turn zero potentiometer. The meter is 4 1/2". The case for the readout module is constructed of drawn aluminum. The sensor's outer body is of aluminum and engineering thermoplastic. The output signal available is 0.10 mV recorder jacks. Standard accessories includes an AC battery charger and a teflon lined telescoping probe, three feet in length for sampling inaccessible places.

Another example photoionization instrument is hand-held and is flash-light-sized. It is 18" long and 2 1/2" in diameter and weighs three pounds. The sensor and readout are in one component. It has a Liquid Crystal Display and a corresponding pulsed audio signal, using an external earphone, whose repetition rate varies with concentration. Rechargeable NiCd batteries work for 16 hours.

Some typical applications listed by the PID manufacturers include:

- General lab and plant surveys
- Leak detection and detection of potential leaks from high pressure lines or solvent storage facilities
- Monitor workplace exposure
- Survey high risk operation and storage areas
- Waste site evaluations

5.7.3 Performance Data

GC sensitivity, range, and accuracy is mainly dependent upon the detector used. The available detectors include electron capture, photoionization, flame ionization, thermal desorption, and flame photometric.

Compounds whose ionization potentials are lower than the lamp ionizing energy will respond to photoionization detection. Molecules whose ionization potentials are up to 0.3 eV higher then a given lamp energy will also respond although with lower efficiency. For maximum selectivity, the lamp with the energy output just capable of photoionizing the species to be detected should be used.

Combining a photoionization detector and a gas chromatograph into one unit enables organic and inorganic compounds to be detected at the ppb and ppm levels with high selectivity. The PID and GC ionizes all compounds with ionization potentials of less than 10.5eV in ranges of 0-2000 ppm, 0-20, and 0-200 (typical). The minimum detectable sensitivity is 1-50 ppb depending on the compound.

The photoionization instrument consisting of two separate units (readout and sensor) is sensitive 0-2 ppm full scale for many species and accurate to 0.1 ppm.

The following compounds are an example of the chemicals from Table 4.1 measured in the 0-20 ppm range; acrolein, acrylonitrile, hydrogen sulfide, and methyl isocyanate. Other examples include: aldehydes, aromatics, benzene, carbon tetrachloride, dimethyl sulfide, ethylene dibromide, formic acid, inorganic gases, hetones, nitrates, organic gases, pyridine, toluene, vinyl chloride. The 0-200 ppm range brings in one more chemical from Table 4.1, ammonia. Styrene and tetraethyl lead are also measured at this range.

The handheld photoionization instrument has a performance of within ± 20% of the maximum concentration (benzene) in the linear range of 0 to 2000 ppm. The detection limit is below 0.05 ppm for benzene. Detectable compounds include all gases and vapors whose ionization potential is below 10.5 eV. Such a range encompasses a very large number of solvent materials including vinyl chloride, hydrogen sulfide, arsine and phosphine.

5.7.4 Advantages

- Versatile system
- Some units are portable (battery operated)
- ppb sensitivity
- Some units are microprocessor controlled
- Detects organics and inorganics
- No flames or support gases
- Quick response
- Alarm options available
- Most units easy to operate

5.7.5 Disadvantages

- Interferences

5.8 MASS SPECTROSCOPY (1, 2, 13, 14, 15)

5.8.1 Principle of Operation

Mass spectroscopy consists of deflecting ionized molecules that have been subjected to a magnetic field and sorting these ions according to their mass/charge ratio. The current intensity detected is proportional to the number of particles in each class. Every compound has a characteristic number of different ions. The mass spectrum is a record of these characteristics. The sample size required is very small, in the order of 1.0 microliter of gas. Specificity is high because individual particle classes are detected with instruments of high reduction capability. The detection limit for SO_2 for example, has been reported in the order of 0.001 microliter. Mass spectrometry has been combined with gas chromatography for the identification of chromatographic fractions and peaks.

5.8.2 Physical Description and Applications

A typical control unit for a mobile monitor is 20" X 31" X 22", while the analyzer unit is 9" X 31" X 22". Together they weigh in the range of 130 - 160 lbs., and use a maximum of 500 watts. An example of a monitor with external components is 51" X 43" X 21", weighing 600 lbs. These external components are a graphics terminal and keyboard, a hard copy unit, a PDP11/03 computer, and a table. Together these other pieces weigh 390 lbs. Some models consist of a core unit to which may be attached various types of front ends and inlet systems. For the purposes of this report, the ambient air analysis type of inlet and front end is assumed to be necessary.

The models studied for this report are designed to be used in either the laboratory or the field, and are adaptable to applications requiring rapid measurement, monitoring or investigation of specific trace components in complex mixtures. Two areas where this technology is useful were listed by a

manufacturer to be animal/human toxicology studies and chemical site surveys. Some models can be used for factory monitoring due to stand-alone operation. No alarm systems were discussed in the samples of promotional literature used for this report.

5.8.3 Performance Data

Low end detection extends down to the ppt concentration levels; for example, the minimum detectable concentration for acrylonitrile in one variety of mass spectrometer is 100 ppt. In another model the detection limit is 2 ppb. As another example, TDI has a detection limit of 10 ppb in both models. A saturated response is usually obtained at some point above 10 ppm, that point varying with the compound and reactant ion. A saturated response implies that all of the reactant ions are replaced by product or trace ions. Quantitative response can be regained by diluting the sample with additional pure reactant gas, or air.

For positive or negative ion detection under a typical spectrum scan, the system noise is not greater than 10 ions/second for a typical monitor. Thus, standard deviation is less than 10 ions/second. The ultra-low concentrations of compounds, such as 10^{-11} or 10^{-12} mole parts, can be detected by mass spectroscopy, but are sometimes masked by an ambient interferent background. A model studied for this report used pulse counting techniques to reduce the system noise level.

Mass spectroscopy can be used to monitor the presence of many classes of compounds, examples being aldehydes, nitriles, inorganic acids, isocyanates, organometallic compounds, sulphur compounds, alkaloids, amides, halides, and explosives. Response time can be as low as 0.5 seconds for some compounds.

5.8.4 Advantages

- Quick response
- Variety of detectable compounds
- Computer-controlled
- Very sensitive and specific
- Small sample size

5.8.5 Disadvantages

- Some models not very portable or compact
- Cost

5.9 HALIDE DETECTOR (1, 16)

5.9.1 Principle of Operation

The sample is drawn through a flexible sampling line to a glass wool filter which removes any gross particulate matter or droplets. It then is drawn into a spark chamber. Gases and spark decomposition products continuously exit from the chamber to a halide trap which is packed with activated charcoal. From this trap, the sample flows to a pump and through a flowmeter. It is then exhausted.

Any halogen compounds in the sample will cause the ultraviolet emission from the spark to brighten. This increase in spectral intensity will be detected by the photocell and will be indicated on the meter. Interpretation of this reading is made by relating the meter reading to a calibration curve based on the specific gas being tested.

5.9.2 Physical Description and Applications

This instrument is 11" x 7" x 7", weighs 13 lbs, and has power requirements of 120 V, 50/60 Hz (also available in 230 V 50/60 Hz and 100 V 50/60 Hz versions). Recorder output is adjustable from 0-10 to 0-50 millivolts.

No alarm options are discussed by the manufacturer. Its primary field of application is by industrial hygienists in industrial solvent cleaning and fine chemical production facilities. It has also proven useful as a process monitor.

5.9.3 Performance Data

Threshold limit concentrations of most halogen-containing compounds are easily determinable on the meter. The instrument also has a range adjust in arithmetic ratios of 1,3 and 10 permitting expanded readings up to 10,000 ppm. Interpretation of readings is determined by use of calibration curves provided with the instrument. The instrument is generally not subject to interference from non-halogenated substances, but it is affected by the presence of sulfur

and cyanogen compounds. Sensitivity to these compounds is an order of magnitude less than sensitivity to halides. Response time is 3 to 5 seconds with a precision of ± 3% and an accuracy of ± 5%. Line voltage changes will have an effect on readings, otherwise stability is approximately ± 5% per day.

Response is a function of the type and number of halogen atoms, with greatest sensitivity obtainable on chlorine compounds.

5.9.4 Advantages

- Portable
- cost

5.9.5 Disadvantages

- Alarm options not available from manufacturer

5.10 ELECTRO-CHEMICAL DIFFUSION (16, 17, 18)

5.10.1 Principle of Operation

The sensors used in each system are diffusion-type electro-chemical gas sensors. The basic detector consists of a sensing electrode, a counter electrode, and electrolyte enclosed together behind a membrane. The toxic gas molecules permeate this membrane and react with the electrolyte, causing a potential change of the sensing electrode (for NH_3 from Table 4.1 and others such as Amines, HCN and CO_2) or a current change between electrodes (for Cl_2, HCl, H_2S, Br_2, and HF from Table 4.1 and others such as H_2, ClO_2, SO_2, CO, AsH_3, PH_3, SiH_4, F_2, I_2 and NO_2). The sensors are specifically designed for each gas to be detected.

5.10.2 Physical Description and Application

Portable models are designed for use in field or factory, and are independent of controller units. A typical portable sensor is 8.5" x 4.3" x 6.8", and weighs 3.4 lbs. This type of sensor can be battery operated when hand-held or can be a fixed monitor with a battery charger unit. The batteries

alone will provide around 20 hours of power. Response time is 10-15 seconds, and an alarm will go off at a point which is adjustable. These portable models can be used in a corrosive environment, an O_2-free environment, and in temperature ranges from -29 °C to 50 °C.

Models which require controller units place the alarm and the meters in a separate place away from the detector. The sensor itself can be located up to 10 feet away from the sensor transmitter. The sensor unit can be located over 2 miles from the controller unit. The controller case can accept up to 8-12 controller or indicator units. Usually one alarm unit will serve up to 12 indicator units and all fit into a rack that is about 2" W x 7" H x 11" D. The detectors require 15-30 Vdc while the controllers need 24 Vdc. Alarms are set by switches on the controller unit, and will go off in case of power failure as well. Response time for these models varies from < 20 sec for HCN monitors to < 6 sec for Cl_2 monitors. These models can also be used in a corrosive environment and an oxygen-free environment. The sensor will operate in a temperature range of -10 °C to 50 °C but the controller unit can withstand -29 °C to 50 °C.

The sensor transmitters are explosion proof, if housed in U.L. approved condulets, and so can be used in hazardous area NEC Class 1, Division 1, Group B, C, and D areas. When used with the specified Factory Mutual approved zener barriers the sensor transmitter is intrinsically safe for use in hazardous areas NEC Class 1, Division 1, Groups A, B, and C. This means it is not necessary to ensure the area is clear of combustible gas prior to opening the sensor electronics.

Both types of monitors have an expected longevity of 3 years.

5.10.3 Performance Data

Ranges vary for sensors monitoring different gases. Typical examples are Cl_2: 0-3 ppm; HCN: 0-30 ppm; NH_3: 0-75 ppm; HCl: 0-9.9 ppm; HF: 0-9.9 ppm; Br_2: 0-9.9 ppm; and H_2S: 0-50 ppm.

Accuracy for the portable models described above is less than ± 10% full scale. Repeatability is given as less than ± 10% also. For the models with separate controller units accuracy is generally ± 5% full scale.

Interference can come from "RFI/EMI" - Radio Frequency Interference and Electro Magnetic Interference. These models are designed to minimize this type of interference, by shielding the system.

Since each sensor is designed for detecting one gas only, the interference from co-existing gases is low. For example, a Cl_2 detector can exist in an environment with 1000 ppm HCl would show zero meter indication from the HCl. if 200 ppm NO were present, it would indicate a meter reading of 0.06 ppm.

They monitor for gases including Cl_2, HCl, HF, F_2, Br_2, ClO_2, I_2, NH_3, HCN, CO_2, SO_2, H_2S, CO, NO_2, H_2, and SiH_4.

5.10.4 Advantages

- Small sensors
  - easily placed in fixed position
  - very portable
- Sensors can be placed far away from controller
- Low interference
- Durable, can operate under harsh conditions
- Alarms already installed
- Continuous unattended monitoring

5.10.5 Disadvantages

- Monitors are specific for one gas
- longer response time than with some techniques

6. INCIPIENT DETECTION AND WARNING SYSTEMS (17, 19, 20, 21, 22, 23)

6.1 INCIPIENT DETECTION

Early detection and warning of airborne emissions which would pose an immediate public health hazard are essential in monitoring the operations of chemical manufacturing and handling facilities.

On-line process monitoring is important to early detection of airborne emissions in the chemical industry. The majority of on-line process monitoring instruments are simple physical sensors. These sensors measure physical properties such as pressure, temperature, density, level and flow. Physical sensors are used rather than sophisticated laboratory instruments because they are extremely reliable, rugged, durable, fail-proof and remain accurate for long periods of time without calibration, inspection or maintenance. Some disadvantages of physical sensors are that they rely on interpretation that is dependent on experience and there is an economic limitation on the number of points to be monitored.

There is a recent trend toward using generalized instruments containing one or more physical sensors that transduce the quantity to be measured to an electronic output and computer system that provides the visible and/or audible output. Economically, this is advantageous because many sensors may share one electronic system. These computerized electronic systems provide the reliability needed for process control and automatic recalibration and verification routines are possible to provide the stability required in process control.

Another direction in improving control analysis technology is to separate the sensor from the readout system, as in remote measurements. Fiber optic chemical sensors are a means of combining early detection with the advantages of remote measurement. Advantages include measurements of hazardous samples without exposure to personnel, multiple station monitoring with one central instrument and numerous optical fibers, and cost-effectiveness because optical fibers are much less expensive than multiple instruments.

Fiber optic chemical sensors can be used to monitor process streams so the movement of hazardous material through the facility is known and loss of material can be accounted for quickly. Simultaneously, they allow real-time reporting of chemical concentrations.

The small diameter of a single fiber and its mechanical strength and flexibility help to make remote measurements possible. High quality optical fibers are available to transmit light very efficiently over ranges of up to half a mile to the sample and back. Standard laboratory spectroscopic procedures can then derive the composition of the sample.

Built-in sensors on chemical storage and transport tanks are currently being considered. These sensors give benefits such as continuous sampling, real-time data, and no sample alteration, and are rather simple in design. They also increase reliability of equipment, provide guidance for maintenance and provide real-time warnings of changes in critical machinery. Basically, these sensors are developed from existing technology in physical sensors. Demands are that they must be small, economic for mass production, rugged, easy to install, and must not need much support equipment.

6.2 WARNING SYSTEMS

Warning systems can be used with almost all monitoring devices. Microprocessor controls can be programmed for audible, visual and telephone warnings.

This report discusses two types of alarm systems. The first alarm system is constructed for use in one application only; the second can be used in many applications.

Some manufacturers of monitoring instruments develop unique alarms for specific instruments. An example is the instrument-specific alarm system for electrochemical sensors. Most electrochemical sensors are available with high- and low-level alarms for each sensor and a trouble alarm for each controller. Usually alarm lights are solid for low-level alarms and flash for high-level alarms. Relays for high, low and trouble alarms will activate circuitry for a remote alarm indicator. Alternately, this relay could shut down gas flow or a process. Records of system status, alarm events, threshold concentration, trouble and system configuration can be produced. Most alarm modules provide a loud audible tone when either pre-set high or low alarm concentrations exist. There are actually three separate indications of an alarm condition: 1) a meter reading; 2) a light indicator; and 3) an audible alarm.

Alarm systems which incorporate data loggers are more versatile and can be used with most meteorological and air quality instruments. Data loggers are suitable for stand-alone operations. They can output data to a printer, cassette recorder, cartridge recorder or other parallel compatible device. They also may be used as telemetry terminals in a distributed monitoring network with an internal data buffer that stores acquired data between interrogations and is linked to the central system via dial phone, dedicated line or radio link.

Data loggers are available to control calibration and other time-dependent functions such as data formatting and alarms. They can handle the automation of remote monitoring sites and can be controlled remotely for all keyboard operable functions including time setting; initiating calibration; altering program selection; and examining current set-up and recurring diagnostics.

Another example of versatile application alarm systems is the data acquisition system that interfaces to a computer. This system is most often a microcomputer-based measurement and control system on a single printed circuit board. It provides a solution to processing analog input data and digital input/output controls. Some data acquisition systems provide sensor signal conditioning, analog multiplexing, analog to digital conversion, digital input/output and serial communications. Some are available as plug-in modules that allow selection of standard signal conditioning modules for direct connection to a wide range of sensors.

The microcomputer scales, linearizes and converts the input data to engineering units and stores the results in random access memory. The data stored in memory are continuously updated.

The computer monitors and controls the system. The outputs can sound alarms or start other processes such as heaters, air conditioners and sprinklers through solid state switching devices. There are many specific interfacing systems available.

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